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Thermal Diffusivity of Carbons and Graphites in the Temperature Range from 1800 to 3300°K

JUNE 1967

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Prepared for BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISIONS
AIR FORCE SYSTEMS COMMAND
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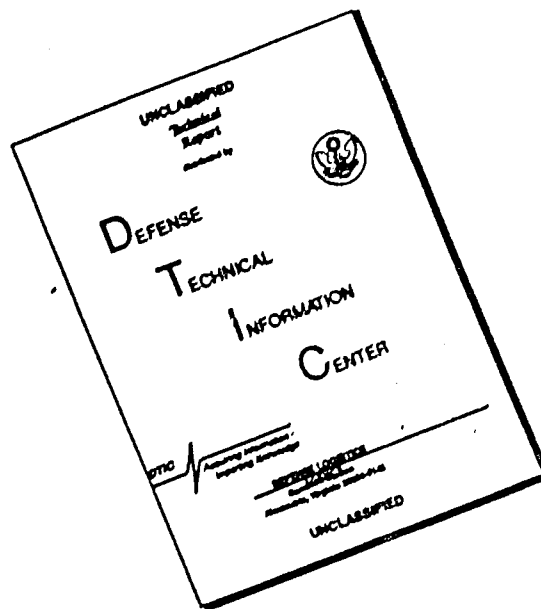
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FOREWORD


This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract No. AF 04(695)-1001.

This report, which documents research carried out from November 1964 to August 1965, was submitted on 8 June 1967 to Captain William D. Bryden, Jr., SSTRT, for review and approval.

The content of this report was first presented as a paper at the Fifth Conference of Thermal Conductivity at Denver, Colorado, in October 1965.


The authors would like to thank J. E. Hove for his continuous interest in the progress of this work as well as many useful discussions. Conversations with W. C. Riley, J. D. McClelland, and J. Slaughter are gratefully acknowledged. Thanks are also extended to D. C. Robinson for technical assistance.

Approved:



W. C. Riley, Director
Materials Sciences Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



William D. Bryden, Jr.
Captain, United States Air Force
Project Officer

ABSTRACT

Improved and new steady periodic heat flow methods for the direct measurement of the thermal diffusivity of carbons and graphites at very high temperatures have been developed. Their main features are techniques that overcome the difficulties arising from the radiative environment with thermal conductance much greater than that of the material under investigation. In addition to the previously reported double disc method, a new technique using multiple radiation shields to suppress the radiative exchange of the critical surfaces of the specimen with the surroundings has been explored. A brief analysis of the thermal driving point impedance of such shields by means of matrix methods is given in conjunction with a description of the implementation of the derived requirements for proper functioning with stacks of tantalum carbide discs.

The thermal diffusivities of various carbons and graphites were determined with these techniques and were found to be essentially independent of temperature throughout the entire range investigated. It is argued that the observed c-direction conduction in pyrolytic graphite is probably not of intrinsic nature, but is at best a small component of the a-direction conduction caused by tilt angle variations of the microcrystallites. It is further suggested that the heat conduction in graphites at high temperatures is substantially of electronic nature, a point supported by Lorenz numbers based on more recent data. The essentially temperature-independent diffusivity of graphite reflects, then, the behavior of ordinary metals above the Debye temperatures.

An unexpected and yet unexplained frequency dependence of the diffusivity was found at extremely low frequencies of the periodic heat flow. It is not clear whether this is a natural phenomenon or an experimental imperfection of the methods employed.

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INTRODUCTION

It is a widely accepted belief that all time-dependent thermal propagation processes in a material are determined by a diffusivity and a conductivity K that are uniquely related by $K = \alpha \rho C_p$, where ρC_p is the specific heat per unit volume at constant pressure. If the specific heat is known, a determination of α is simply an indirect method for obtaining the conductivity, a concept frequently used in the classification of thermal propagation parameters. Since the measurement of K is often the easier one at high temperatures, the determination of α appears rather superfluous.

This widely accepted belief is based on the assumption that the process of heat propagation at any point within a material can be fully described by a pair of simple equations, which relate the flux q to the temperature gradient and its divergence to the rate of temperature change.

$$q = K \text{ grad } T$$

$$\text{div } q = \rho C_p \partial T / \partial t$$

and from which the above-mentioned relation between K and α originates. There are at least three reasons why such a pair of equations might be insufficient to fully describe the thermal propagation process in materials.

1. In heterogeneous materials, a characteristic conductivity of the composite may be defined provided that the dimensions of the specimen remain large in comparison with the dimensions of the aggregate particles. However, the diffusivities of the elements of the composite do not simply average out, but appear in independent arguments of the solutions. In consequence, a common diffusivity related in the normal fashion to the specific heat and the conductivity of the composite does not exist.

2. The simple Fourier equations entirely omit inertial phenomena, implying, for example, that the heat flux is "instantaneously" proportional to the temperature gradient at any point within the material. This, of course, is incorrect in principle, as was already known to Maxwell and has been more recently considered, for example, by Vernotte (Ref. 1). If a relaxation time exists, a second time derivative of the temperature must be added, which results in a typical wave equation. In consequence, a short heat impulse will not diffuse into the material, but will lead to oscillations. Such processes should be noticeable where the frequency--relaxation time product $\omega\tau$ approaches unity. For typical phonon relaxation times on the order of 10^{-12} sec, such phenomena will not occur at frequencies very much less than 10^{11} cps, so that under ordinary circumstances such relaxation times may indeed be omitted in the equations (Ref. 2). However, it should be mentioned that for certain thermal blast conditions, relaxation phenomena may have to be considered.
3. Very slow relaxation processes can occur when a thermal gradient initiates a mass transport. This phenomenon is known as the Soret effect, and it leads normally to a concentration gradient. Such processes are well known in liquids and are usually considered in the theories of irreversible thermodynamics (Ref. 2). There is no known reason why such processes should not occur in solids, particularly at high temperatures, where the mobility of atoms becomes quite noticeable (Ref. 3). Thermal diffusion in a temperature gradient in solids has indeed been observed (Ref. 4). The effect of mass transports in a temperature field on the conductivity is obvious. As the moving mass carries a heat of transfer, the added heat fluxes will initially increase or decrease the conductivity, depending on the direction the additional heat flux takes in a static temperature field.

Normally, after some time, a concentration gradient is built up sufficient to stop the mass flow entirely, so that only the ordinary heat flux remains. Consequently, the initial and the final conductivity can differ significantly. In a periodically changing temperature field, only an insufficient concentration gradient will be generated, which stops the mass transport only partially and results in frequency-dependent conductivity and diffusivity.

There is still no direct evidence for such thermal conductivity processes in solids. This may, however, be because the preponderance of work on thermal conduction in solids is concerned with steady state conductivity, which, by its very nature, determines only the state of affairs after all transient phenomena have died out. Only transient or steady periodic thermal propagation data can yield information concerning time-dependent phenomena. Any attempt to obtain from the relation $K = \alpha \rho C_p$ a diffusivity that uniquely determines time-dependent conduction processes is futile.

Probably the most drastic demonstration of the existence of such phenomena as described above is the appearance of a frequency-dependent "diffusivity" with steady periodic thermal flux variations, if the analysis is based only on the ordinary Fourier theory. Obviously, a simple relation between such a diffusivity and the specific heat and conductivity cannot exist.

In general, then, conclusions from steady state measurements on time-dependent processes, transient or periodic, must be preceded by direct investigations into the behavior of the diffusivity. Only if the diffusivity is clearly a frequency-independent constant will a normal relation between α and K exist. Even though in the majority of cases, and particularly at low temperatures, normal relations will prevail, there is no basis for the assumption that this will be true for all cases.

In a sense, then, the measurement of diffusivity in solids is more than an indirect method for the determination of conductivity. It is a direct means of revealing conduction phenomena inaccessible by ordinary conductivity measurement methods.

In this study we are concerned with appropriate techniques for extending the steady periodic flux methods to very high temperatures, and we illustrate the techniques with measurements on a quasi-isotropic carbon (CEP) and strongly anisotropic pyrolytic graphite (PG).

II. EXPERIMENTAL TECHNIQUES

A. DESIGN CONSIDERATIONS

If a single slab of material, maintained at some mean temperature, is subjected to a periodic heat flux on one side, the temperatures of both the front face and the back face will vary periodically. The relation between the amplitude and phases of the temperature variations can be expressed in terms of a complex attenuation. The attenuation is not only a function of the material properties, but depends strongly on the thermal load, produced mainly by radiation from and to the backside of the slab. Obviously, the material slab is in series with the purely resistive element of the gap between the backside of the material slab and the environment.

The relation between the complex attenuation and the characteristic parameters of the material and the radiative environment is most readily obtained for such series arrangements by the matrix product method. It is well known that the behavior of the materials, as well as that of the radiation gap, can be fully described by square matrices with elements given, for example, in Ref. 5. Using this method, we find that the attenuation Z of the temperature wave between the frontside and the backside of a single slab under the condition of a radiative or convective load at the backside is

$$Z = \cosh \hat{B} + Nu \sinh c \hat{B}$$
$$\hat{B} = B(1 + j), \quad j = \sqrt{-1}, \quad \sinh c \hat{B} = \hat{B}^{-1} \sinh \hat{B} \quad (1)$$

where B is the thermal thickness of the slab expressing the actual thickness in terms of the wavelength λ of the thermal wave in the material. It is this parameter from which the diffusivity α must be extracted on the basis of the relation

$$B = 2\pi l / \lambda = (\omega/2\alpha)^{1/2} l \quad (2)$$

where ω is the angular frequency of the thermal wave. In addition to B, Eq. (1) contains the Nusselt (or Biot) number Nu characterizing the effect of heat losses at the backside. The Nusselt number expresses the losses in terms of the conductance of the material slab. At very high temperatures this number has a profound effect on the measured results. In the case of pure radiation exchange between completely black surfaces, the loss number is simply (σ = Stefan-Boltzmann constant)

$$Nu = 4\sigma T^3 l / K \quad (3)$$

On this basis, a PG slab 1 mm thick exhibits at 3000°K a Nusselt number of approximately 6, which clearly indicates the significance of this number. In general, neither will the material be black nor will the heat losses be entirely due to radiation if a gaseous atmosphere must be used. It is clear that either the Nusselt number must be determined from the experiment or provisions must be made for eliminating its effect by suppressing the heat loss from the backside.

The effect of large Nusselt numbers can readily be seen from a polar presentation of Eq. (1) in the form

$$Z = |Z| e^{j\phi} \quad (4)$$

where $|Z|$ is the magnitude and ϕ the phase of Z. The loci of Z are plotted in Figure 1. We recognize that with increasing frequency, which increases B, both magnitude and phase shift of the attenuation increase regardless of the value of the Nusselt number. The effect of the Nusselt number, however, is to increase the magnitude of the attenuation and to decrease the phase shift. In any event, large Nusselt numbers greatly change the Z vector from its value $\cosh B$ without heat loss. On the other hand, any specific pair Nu, B results in a unique Z vector. If, therefore, the magnitude and phase of the attenuation are measured, both Nu and B will be uniquely determined. The determination of the magnitude of the attenuation Z involves accurate measurements of the temperature amplitude at the frontside and backside

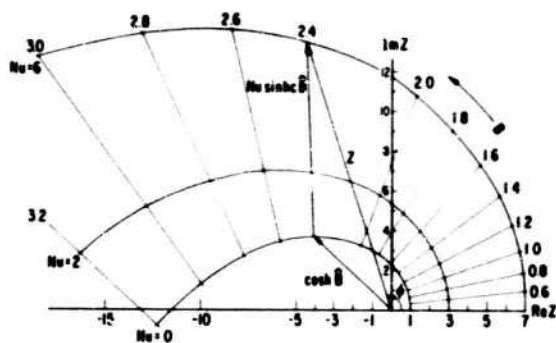


Figure 1.
Loci of temperature attenuation Z in the complex plane.

Figure 2.
Influence of Nusselt number Nu on the relation between phase shift ϕ and thermal thickness B of a slab of material.

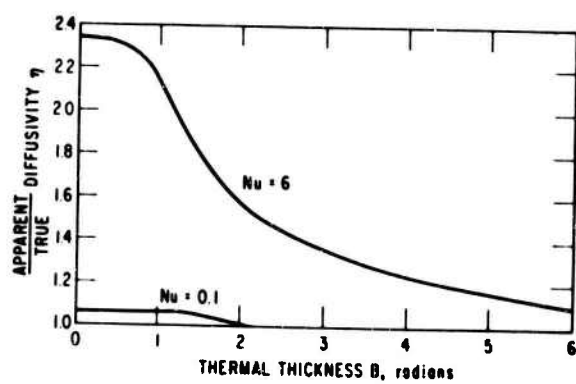
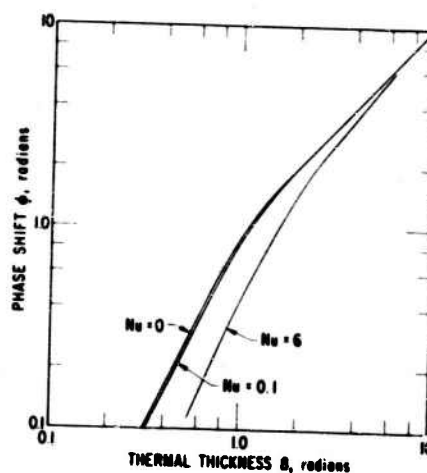


Figure 3.
Errors in diffusivity if heat losses are neglected in the analysis of phase shift data.

of the specimen, a task that is notoriously difficult and should be avoided. At very high frequencies the influence of the Nusselt number on the phase disappears (Figure 2), but the associated large attenuation prevents experimental use of this region. Neglecting the effect of Nusselt numbers entirely leads to very large errors (Figure 3). The only correct approach for avoiding amplitude measurements is to suppress the heat loss at the backside altogether. This can be accomplished in two different ways:

1. The heat loss can be compensated by a completely symmetrical arrangement (Ref. 6).
2. The heat exchange can be suppressed by an appropriately designed heat shield. It is this method with which we are concerned here.

With an effective $Nu = 0$, the phase lag alone defines the thermal thickness B , which, in turn, determines the diffusivity α .

B. EXPERIMENTAL DETAILS

We have previously reported a new technique to determine α of materials at very high temperatures (Ref. 6). Elimination of the thermal load at the backside of the slab under investigation was accomplished by a symmetrical arrangement in which two discs, operating back to back, were subjected to the same periodic conditions. This method has since been greatly improved. One of the conditions for proper functioning is identical amplitudes and phases of the periodic temperature variations on the frontside of both slabs. Identical fluxes are not sufficient because differences in the frontside Nusselt numbers (due to different emissivities) may involve both amplitude and phase of the temperature variations. To avoid these difficulties, we developed a different technique, which uses a stack of heat shields at the backside of a single disc to suppress the heat exchange to a negligible amount. We concern ourselves in the following mainly with details of this technique, the results of measurements, and their significance.

The experimental setup was essentially the same as that previously used with the double disc method. A schematic presentation of the new experimental arrangement is shown in Figure 4a. Figure 4b is a close-up photograph of the apparatus. The specimen was again imaged back onto itself after modulation of the radiation; this re-imaging caused variations of the specimen's surface temperature on the order of 0.1°K . Rather than extracting a mean value of the phase delay from graphical recordings, we used a precise digital technique. The time interval between the zero crossings of the two traces was counted with the time interval measurement technique available on digital counters. By a slight modification, we could disengage the reset of the counter after each time interval measurement so that up to 50 totals of the time interval measurements could be printed out, from which a highly smoothed mean value of the delay time could be obtained. In some of the experiments we employed a modified optical system. It produced an intermediate image of the sample outside the furnace, where a field stop prevented the return of any modulated radiation originating from parts of the furnace other than the specimen. No significant difference in the results was observed, however, which indicates that the surroundings of the specimen in the furnace presented a sufficiently large heat sink to prevent wall temperature variations.

The main feature of the new method is the use of heat shields to suppress the heat loss from the backside of the sample. The effect of a heat shield is a high thermal load impedance. If properly designed, it will reduce the initial Nusselt number to a small and insignificant fraction. The analysis of such stacked heat shields with the matrix method is tedious. For this reason, only the most important aspects are mentioned here.

If the heat capacity of the thermal resistance of the shield material is vanishingly small, then the load impedance of a stack of n elements with small radiation gaps is simply n times the load impedance of a single gap. Accordingly, the Nusselt number is effectively reduced to Nu/n . Unfortunately, such conditions are difficult to obtain at high temperatures with useful refractive materials and geometries. In

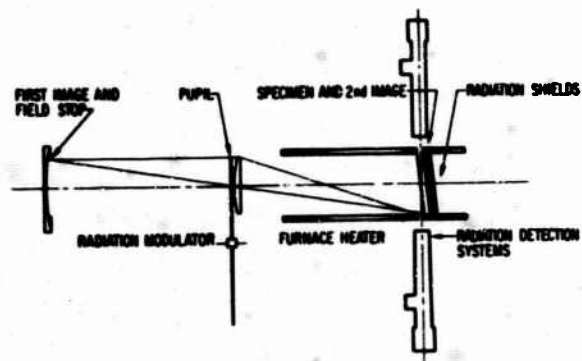


Figure 4a.
Schematic drawing of optical arrangement.

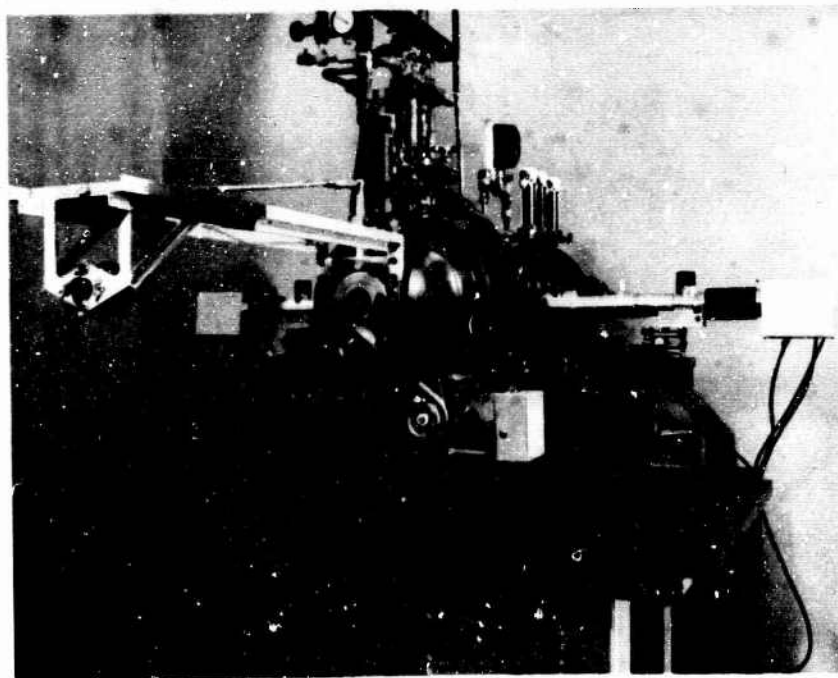


Figure 4b.
Apparatus with modified optical system.

consequence, a stack of radiation shields may show a driving point impedance whose attenuation is insufficient and whose phase factor cannot be neglected. Figure 5 illustrates such a case. The apparent diffusivity is lower than that of a single disc without a shield, but increases consistently with frequency. The analysis of this heat shield confirms this behavior and correctly indicates that such a heat shield would fail even at frequencies as low as 0.0018 cps. It also becomes clear that there is little chance of building a successful heat shield unless much thinner discs of more conductive materials, capable of standing the extremely high temperatures, can be found. Our efforts have finally proved successful with tantalum carbide elements, which we produced by sandwiching tantalum metal discs between carbon discs and exposing the stacks to temperatures of 2000°C.

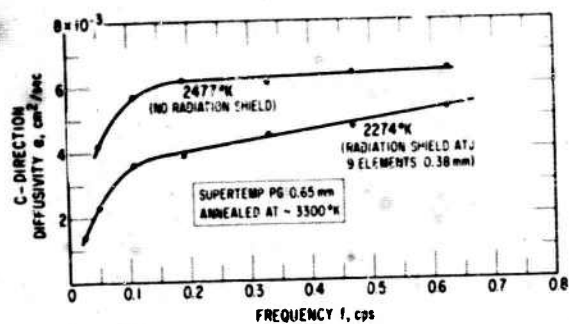
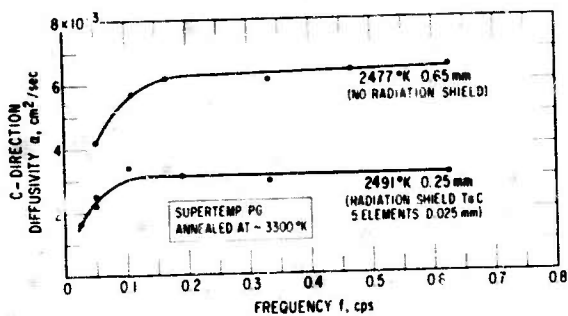


Figure 5.

Characteristic effect of an improperly designed heat shield.

Figure 6.
The diffusivity of pyrolytic graphite in the c-direction. The lower curve shows the effect of radiation loss suppression by a properly designed heat shield.



III. RESULTS

We begin the report of the results with some measurements of the diffusivity of pyrolytic graphite (PG) in the c-direction (Figure 6), which illustrate the points previously made. The upper curve shows a single disc measurement without heat loss suppression. The lower one shows the result obtained with a stack of tantalum carbide shields. The difference between the flat parts of the curves corresponds roughly to a complete elimination of radiation exchange.

Below 0.15 cps, α becomes frequency dependent. The effect occurs in curves both with and without heat shields. Indeed, this behavior is found at all temperatures and with all carbon and graphite materials investigated. All of the α values are within the range estimated from reported conductivity values [$\alpha = 0.0015$ to $0.0035 \text{ cm}^2/\text{sec}$ (Ref. 7) and $\alpha = 0.00075 \text{ cm}^2/\text{sec}$ (Ref. 8) at 2500°K].

The frequency dependence of α brings us back to our introductory remarks concerning the appearance of a frequency-dependent diffusivity caused by transport phenomena neglected in the differential transport equations. We have investigated the low frequency portion of the curve quite extensively but the evidence, as yet, does not permit us to make a definite statement in this respect. Experimental variations definitely alter the shape of the low frequency portion of the curve and may even reverse its slope. It is not yet clear to what this effect should be attributed; further exploration is needed. It is mainly for this reason that for the present time we delete the low frequency portion of the curves from our considerations and concern ourselves with α values of only the flat sections of the curves. Figure 7 shows the temperature dependence of the α values for the c-direction of PG. Except for the very highest temperature point, where possibly the onset of the vacancy effect (Ref. 9) occurs, the diffusivity is essentially temperature independent. We compare this with similar measurements of CEP type carbon (Figure 8), which shows practically the same behavior despite the fact

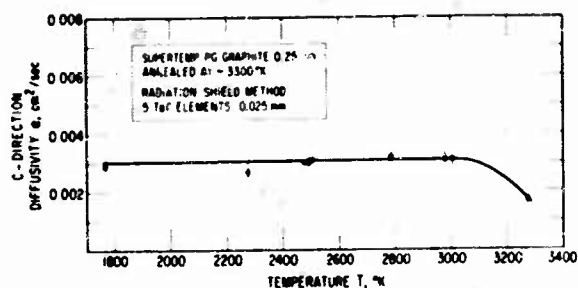


Figure 7.
The diffusivity of pyrolytic graphite in the c-direction as function of temperature.

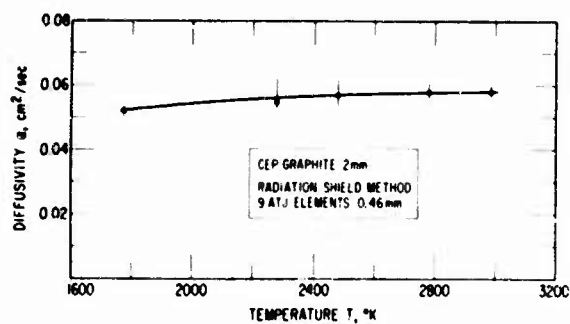


Figure 8.
The diffusivity of CEP type graphite (carbon) as a function of temperature.

- that the materials structure is quite different. Measurements on other graphite materials not yet completed seem to confirm this general behavior. Similar results have been reported by Juul (Ref. 10), who used transient techniques for a variety of polycrystalline graphites. It remains, however, remarkable that a highly ordered material such as PG exhibits, on a different level, the same qualities.

IV. DISCUSSION AND CONCLUSIONS

We are, of course, aware that the conduction process in carbons and graphites is affected by a variety of factors, such as microstructure and its regenerative nature, heat treatment, and cracks (Ref. 7). However, here we will look briefly at consequences resulting directly from the lattice structure and its anisotropy. This is most conveniently done in terms of the reciprocal lattice (σ -space), the structure of the Brillouin Zone (BZ), and the constant frequency surfaces resulting from the characteristic dispersion equations. To find, for example, the specific heat, we simply sum up the contributions of each point in the σ -space of the BZ. In the case of lattice conductivity, these contributions must be weighted according to the group velocity and the lifetime of the modes of vibration. We see this clearly from the equations for the heat capacity per unit volume C_v and for the corresponding thermal conductivity when they are written in parallel form

$$C_v = k \sum_j \int E(\omega) \iint \frac{dS}{|\Delta_\sigma \omega| (2\pi)^3} \quad (5)$$

$$K_s = k \sum_j \int E(\omega) \iint \frac{v_s^2 \tau dS}{|\Delta_\sigma \omega| (2\pi)^3} \quad (6)$$

where the double integral in Eq. (5) is simply the density of modes at a given frequency per unit frequency interval and unit volume. $E(\omega)$ is the Einstein specific heat function, k is the Boltzmann constant, v is the group velocity, and τ is the relaxation time. The subscript j refers to the various acoustical and optical branches, the subscript s to one of the selected principal axes of the lattice structure; otherwise the symbols have the usual significance. The double integration is carried out over constant frequency (ω) surfaces.

If we form from these equations the diffusivity α , we obtain $\alpha_s = \langle v_s^2 \tau \rangle$ representing some grand mean of weighted averages of the $v_s^2 \tau$ products within the BZ of all branches. In the simplest isotropic case, the group velocity v and the relaxation time τ are everywhere the same and independent of the direction, which implies that the ω -surfaces are spherical. We obtain the usual Debye results: $\alpha_s = \langle v_s^2 \rangle \tau = v^2 \tau / 3 = \Lambda v / 3$. If the group velocity is identical to the phase velocity of sound, we can define a meaningful relaxation length Λ . In general, however, this is not the case.

However, certain conclusions of very general nature concerning the temperature dependence of the characteristic thermal parameters can still be drawn. They are most readily obtained from illustrations.

In order to save time, we immediately consider the Brillouin Zone and ω -surfaces of the graphite structure. The best known illustration (Figure 9) is the one by Krumhansl and Brooks (Ref. 11). Since the unit cell of graphite contains four atoms, there should be 12 acoustical and optical modes. After doubling the height of the BZ in the Z-direction in consideration of the degeneracy at the top and bottom, we are left with three acoustical and three optical branches, so that, in principle, six different ω -surface structures exist. While sufficient for the discussion of the properties of specific heat, the above picture cannot be used for a discussion of thermal conductance because in its simple form it violates the principle that the ω -profiles must end normally on the BZ surfaces. If we calculate the profiles from the detailed theory, this imperfection disappears. In Figure 10 we show the true behavior. Typical profiles are shown, all of which end properly on the BZ surface. This theory has more recently been modified (Ref. 12) by the introduction of a strong dispersion in the planar direction due to bond bending. The overall picture, however, remains the same; except for the lowest frequencies, the ω -surfaces rapidly assume cylindrical character. The general consequences discussed here therefore remain the same.

Figure 9.

The Brillouin Zone for the graphite lattice. The ellipsoid is a simplified surface of constant frequency according to the theory of Krumhansl and Brooks for the specific heat.

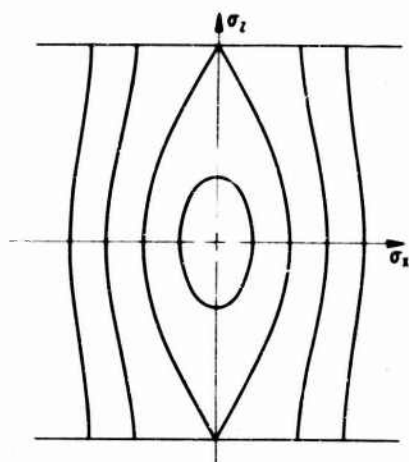
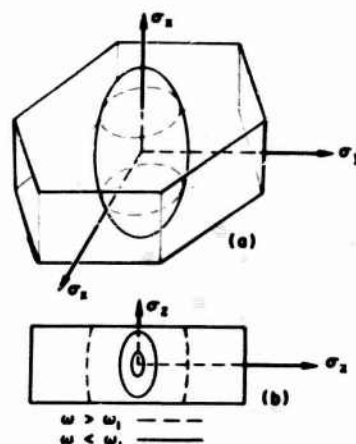
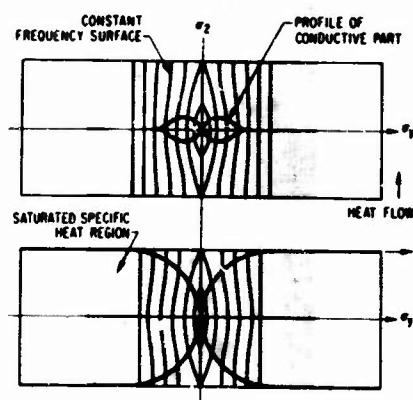


Figure 10.

Details of profiles of constant frequency surfaces near the center of the Brillouin Zone, required for the discussion of thermal conductivity.

Figure 11.

Schematic drawing of the Brillouin Zone of graphite with profiles of constant frequency surfaces. The strong lines enclose the equivalent conduction part of the zone, the shaded part indicates regions (nearly) saturated in specific heat at some intermediate temperature. The upper diagram refers to c-direction conduction, the lower one to conduction parallel to the planes of the graphite lattice.



The main contribution to the conduction comes from the parts of the ω -surfaces where the group velocity has a significant component in the selected direction. For a direction parallel to the planes there is a large contribution coming from almost all ω -surfaces. For the direction perpendicular to the planes the main contribution comes only from ω -surfaces close to the center. Some very slight contribution may also come from the left and right sides of the BZ. Actually, this region is very small, so its contribution to the conductivity is neglected. To indicate the contribution in the vicinity of each ω -surface, we have marked out symmetrically to the horizontal axis in Figure 11 the fractional participation of zone regions to the conduction process. This fraction has an exact meaning; within the BZ exist points where the product $v_s^2 \tau$ reaches a maximum value. Any other product is measured then by a distribution function $\mu \leq 1$. The fraction of modes of frequency ω that contribute "fully" to the conductivity is

$$\bar{\mu}(\omega) = \frac{\iint \mu \, dS / |\nabla_{\sigma} \omega|}{\iint dS / |\nabla_{\sigma} \omega|} \quad (7)$$

This is the function that produces for three-dimensional Debye lattices the factor 1/3 and for two-dimensional Debye lattices the factors 1/2 and 0, parallel and perpendicular to the planes, independent of ω . In the case of PG, $\bar{\mu}(\omega)$ will be very small in the c-direction for higher frequencies, as indicated in Figure 11. The total of these fractions over all frequencies marks out the equivalent conductive portion of the BZ. To be actually conductive, this zone must be occupied by phonons. They contribute a fraction $E(\omega)$ of the specific heat available for each frequency. The shaded zone indicates where the saturation is essentially completed. The volume of the saturated area expands with increasing temperature. From the picture shown on the left side, we immediately conclude that the conductivity reached its maximum value far below temperatures where the specific heat function covers the entire zone and the specific heat approaches its maximum.

It is further evident that any conclusion from conductivity data on relaxation lengths in anisotropic materials must be drawn with considerable caution. Even if there were a relaxation length of considerable magnitude, say, due to crystallite boundary effects, its mean value over the whole BZ would be very small, due to the small conductive fraction of the zone. Such mean values, which one obtains by indiscriminate use of the relations for the isotropic cases, have no simple physical meaning in the anisotropic case.

Finally, we should note that regardless of the type of scattering mechanism due to static imperfections, the conductivity can show a maximum value only at the highest temperatures and can never show a peak in some intermediate temperature region. It is evident that the effect of a temperature-dependent phonon-phonon interaction is a contraction of the conductive zone at elevated temperatures, which, in turn, must finally lead to a decreasing conductivity. Indeed, once the contraction sets in, it increases as the temperature rises, extinguishing the conductive zone more and more.

The behavior of the diffusivity as a function of the temperature cannot always be interpreted so simply, because the total diffusivity cannot be obtained from the sum of the diffusivities of the individual branches, as is the case for the specific heat and the conductivity. At sufficiently high temperatures, however, where the specific heats of all branches are saturated, α is the mean value of the diffusivities of the individual branches. In this region, α reflects the behavior of the conductivity directly.

Thus far, we have discussed the conductance contribution of only one branch. To explain the essentially temperature-independent high temperature conductivity of a material like graphite after a drop of the conductance at intermediate temperatures on the basis of phonon conductance only, one is forced to accept the idea that at least one of the branches is not subject to thermal interactions. The static imperfections would indeed level out the conductivity at high temperatures. However, since direct phonon interactions have to occur between phonons of different branches, it is difficult to see how one branch can survive while others suffer from rapid thermal extinction of their conduction properties.

The nearly temperature-independent conductivity and diffusivity at high temperatures are therefore likely to be of different origin.

Before we examine this point further, however, we must consider more closely the nature of the conductivity in the c-direction. Pyrolytic graphites are polycrystalline solids with an unusual degree of preferred orientation. However, the orientation is by no means ideal. Inclination angles as great as 20 and 30 deg relative to the symmetry axis are readily found, even in heat-treated PG specimens. Guentert and Klein (Ref. 13) arrived at some significant conclusions concerning the effective anisotropy ratio for thermal and electrical conductivities and its relation to the true intrinsic anisotropy. For materials heat-treated at 3000°C and the highest orientation index of 200, intrinsic anisotropy ratios of more than approximately 10 simply cannot be observed. Higher observed effective anisotropic ratios do not reflect the true anisotropy ratio, because a substantial component of the a-direction conduction is thrown into the c-direction by tilt angle variation. Regardless of the value of the intrinsic anisotropy ratios, the effective ratio is limited due to tilt angle variation. Slack (Ref. 14) concluded that ideally ordered graphite might exhibit intrinsic thermal conductivity anisotropy of possibly 1000 even at 300°K. Such ratios cannot be observed with materials subjected only to the above-mentioned heat treatment. Taking the lack of crystal perfection into account, we must conclude that probably none of the presently available c-direction conductivity data give reliable information about the intrinsic c-direction properties of ideal graphite. The observed c-conductivity might often be nothing other than a small fraction of a-direction conductivity turned into the c-direction by tilt angle variation.

Tilt angle variation alone would lead to a temperature-independent effective conductivity anisotropy, which, as yet, has not been found. The observed c-direction conductivity does not normally exhibit the steep increase of the a-conductivity at temperatures below 1500°K; consequently, the observed data (Ref. 7) indicate anisotropy ratios from 400 to 1000 at room temperature -- ratios that, as already mentioned, cannot even be attributed to tilt angle variation, but must be due to the faulty c-direction

flow (i. e., lifting of the radiation shorts of cracks at lower temperatures, etc.). At high temperatures in the range of the flat portions of the conductivity curves, however, anisotropy ratios of about 35 (Ref. 7) could be understood to be caused by tilt angle variation of a-conductance into the c-direction if the intrinsic anisotropy ratio is very high and a sufficient heat treatment of the material has been carried out. If this is correct, then the flatness of the normal c-direction conductivity simply reflects the flatness of the a-direction conductivity. Therefore, from here on we need only concern ourselves with the interpretation of the flatness of the a-direction conductivity at high temperatures.

We have already pointed out that the conduction by phonons alone, barring extraordinary effects, does not lead to temperature-independent conduction at high temperatures.

The possibility of high temperature conduction in solids by electrons and holes has long been recognized (Ref. 15) as leading most readily to a temperature-independent conduction at high temperatures. It is now quite definitely established (Ref. 16) that both types of carriers exist in PG. The idea of a substantial electronic thermal conduction at high temperatures has, however, been rejected (Ref. 17), since previous data of the electric and thermal conduction did not lead to Lorenz numbers sufficiently close to the theoretical Sommerfeld value. An analysis of more recent data (Ref. 7) on PG indicates, however, that the gap is closing.

Table 1. Lorenz Numbers for Pyrolytic Graphite at High Temperatures

L, $(k/e)^2$	T, °K	Data From	Material
23	2000	Hove, Ref. 17	PG a-direction
10	2477	Pears and Allen, Ref. 7	PG a-direction
6	--	Klemens, Ref. 18	Graphite (theory)
3.29	2	Klein, Ref. 19	PG a-direction
3.29	--	Sommerfeld Value	

The experimental L values at high temperatures are still considerably larger than the Sommerfeld value. However, there is nothing sacrosanct about this value, as Klemens (Ref. 18) pointed out. Only in the case of complete degeneracy of the electron gas at very low temperatures should the Sommerfeld value be approached, which indeed occurs (Ref. 19). In the nondegenerate case at high temperatures and under certain simplifying assumptions about the band structure of graphite, Klemens (Ref. 18) obtained a much higher value. The value is subject to the condition that the mean free path is independent of energy, a requirement readily fulfilled in grain boundary scattering. For certain types of electron--phonon interactions this is also true for strictly two-dimensional lattices. Since more detailed knowledge of the electronic band structure of graphite is now available (Ref. 16), indicating the existence of bipolar conduction in graphite, further corrections of the theoretical Lorenz number must be expected.

In any event, the values of Table 1 indicate that the possibility of a substantial, and perhaps pure, electronic heat conduction in graphite at high temperature can no longer be refuted. The presence of bipolar electronic conduction may explain the fact that temperature-independent thermal conductance coupled with temperature-proportional electrical resistance results in a temperature-independent Lorenz number at high temperatures.

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13 ABSTRACT Improved and new steady periodic heat flow methods for the direct measurement of the thermal diffusivity of carbons and graphites at very high temperatures have been developed. Their main features are techniques that overcome the difficulties arising from the radiative environment with thermal conductance much greater than that of the material under investigation. In addition to the previously reported double disc method, a new technique using multiple radiation shields to suppress the radiative exchange of the critical surfaces of the specimen with the surroundings has been explored. A brief analysis of the thermal driving point impedance of such shields by means of matrix methods is given in conjunction with a description of the implementation of the derived requirements for proper functioning with stacks of tantalum carbide discs. The thermal diffusivities of various carbons and graphites were determined with these techniques and were found to be essentially independent of temperature throughout the entire range investigated. It is argued that the observed c-direction conduction in pyrolytic graphite is probably not of intrinsic nature, but is at best a small component of the a-direction conduction caused by tilt angle variations of the microcrystallites. It is further suggested that the heat conduction in graphites at high temperatures is substantially of electronic nature, a point supported by Lorenz numbers based on more recent data. The essentially temperature-independent diffusivity of graphite reflects, then, the behavior of ordinary metals above the Debye temperatures. An unexpected and yet unexplained frequency dependence of the diffusivity was found at extremely low frequencies of the periodic heat flow. It is not clear whether this is a		

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natural phenomenon or an experimental imperfection of the methods employed.

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